

Separating *Para* and *Ortho* Water**

Daniel A. Horke, Yuan-Pin Chang, Karol Długołęcki, and Jochen Küpper*

Water exists as two nuclear-spin isomers, *para* and *ortho*, determined by the overall spin of its two hydrogen nuclei. For isolated water molecules the conversion between these isomers is forbidden and they act as different molecular species. Yet, these species are not readily separable, and little is known about their specific physical and chemical properties, conversion mechanisms, or interactions. Here we demonstrate the production of isolated samples of both spin isomers in pure beams of *para* and *ortho* water, with both species in their respective absolute ground state. These single-quantum-state samples are ideal targets for unraveling spin-conversion mechanisms, for precision spectroscopy and fundamental-symmetry-breaking studies, and for spin-enhanced applications, e.g., laboratory astrophysics and -chemistry or hypersensitized NMR experiments.

Significant efforts have been undertaken to separate and study the nuclear-spin isomers of water, motivated by their importance in a wide variety of scientific disciplines. These range from the astronomical importance of the *ortho-para* ratio [1, 2, 3, 4, 5], to studies of nuclear-spin conversion [6, 7], selection rules and reactive collisions [8, 9, 10] or symmetry breaking [11]. Spin-enriched samples furthermore would allow for hypersensitized NMR experiments *via* polarization transfer reactions [12, 13, 14]. However, unlike other small polyatomic molecules exhibiting spin isomerism, such as fluoromethane or ethylene [15, 16], which were spin-isomerically enriched using the light induced drift technique [7], this has not been achieved for water. Separation through selective adsorption on surfaces was reported [17], but these results remain controversial and could not be reproduced [18, 19, 20, 21]. Thus, studies of spin-conversion dynamics in water have been limited to water embedded in rare gas matrices, with relative spin populations modified by the sample temperature [22]. A recent study investigated nuclear-spin conversion in the gas-phase using cavity ring-down spectroscopy and found no spin conversion for water monomers [23], highlighting the ability of the *ortho-para* ratio to conserve the history of formation of

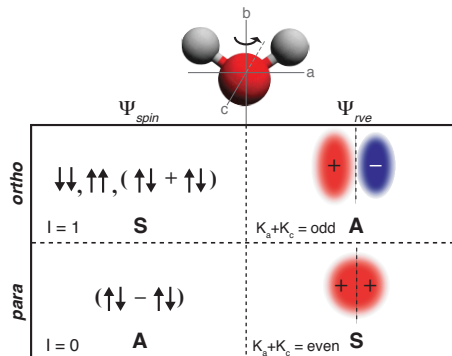


Figure 1: Water spin isomers. The necessity for an overall antisymmetric wavefunction requires that the symmetric (S) spin combinations Ψ_{spin} of *ortho* water combine with an antisymmetric (A) rovibronic eigenstate Ψ_{rve} , and *vice versa* for *para* water.

a water sample in the absence of collisions.

Recently, the production of a single spin isomer of water in a magnetic-hexapole-focuser setup was demonstrated [24]. One of the magnetically active spin projections ($m = +1$) of ground-state *ortho* water was magnetically focused into the interaction volume, while all other spin-projection states were defocused or diverged unaffected by the field. The purity of the produced *ortho* beam was later evaluated as 93 %, with simulations suggesting an upper limit for the achievable purity of 97 % [24, 25].

Here, we experimentally demonstrate the production of pure samples of both, *para* and *ortho* water, the latter further separated into its $M = 0$ and $M = 1$ angular momentum projections, in the gas-phase. The produced single-quantum-states are ideally suited for further experiments on nuclear-spin conversion under collision-free conditions, nuclear-spin-dependent reactivity [8], trapping of single spin-isomer samples in electromagnetic traps [26] or cold matrices [25].

Nuclear-spin isomers arise from the indistinguishability of identical protons, each of which can have its nuclear spin ($i = 1/2$) *up* ($m_i = +1/2$) or *down* ($m_i = -1/2$). Conversion between different nuclear-spin isomers is considered forbidden and the spin isomers can be thought of as different molecular species. In the case of water the nuclear spins of the two equivalent protons can be combined in four different ways, shown in Figure 1. These combinations are grouped into one antisymmetric and three symmetric nuclear-spin wavefunctions, termed *para* ($I = 0$) and *ortho* ($I = 1$), respectively. The symmetrization postulate (Pauli principle) requires an overall antisymmetric wavefunction with respect to exchange of the two fermionic hydrogens. This constrains the allowed combinations of rovibronic eigenstates (Ψ_{rve}) with spin configurations (Ψ_{spin}), i. e., the product of the two corresponding symmetry species

[*] Dr. D.A. Horke, Dr. Y.-P. Chang, K. Długołęcki, Prof. Dr. J. Küpper
Center for Free-Electron Laser Science, DESY
Notkestrasse 85, 22607 Hamburg (Germany)
E-mail: jochen.kuepper@cfel.de
<http://desy.cfel.de/cid/cmi/>

Prof. Dr. J. Küpper
The Hamburg Center for Ultrafast Imaging
Luruper Chaussee 149, 22761 Hamburg (Germany)
Department of Physics, University of Hamburg
Luruper Chaussee 149, 22761 Hamburg (Germany)

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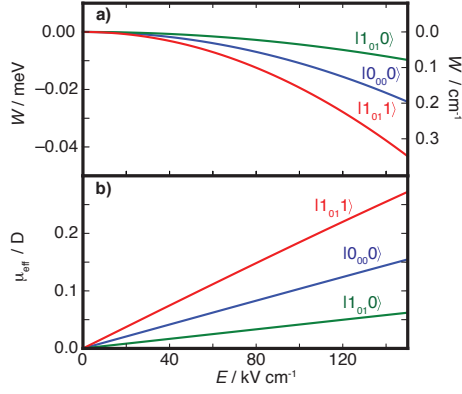


Figure 2: Calculated a) Stark-energy shifts W and b) effective electric dipole moments μ_{eff} for the absolute ground states of *para* and *ortho* water as a function of electric-field strength E .

must be antisymmetric regarding this exchange. Under the conditions of a cold molecular beam, all molecules reside in the ground electronic and vibrational state, both of which are totally symmetric. Therefore, the restrictions are on the rotational levels corresponding to each spin isomer. Relative abundances are determined by the spin degeneracy for each symmetry.

To spatially separate the spin isomers we exploit the different rotational states occupied by *para* and *ortho* water and the corresponding differences in their dc Stark effects. The rotational quantum states of the asymmetric rotor, i. e., water, can be classified by $J_{K_a K_c} M$, with the total angular momentum quantum number J , the projection labels K_a and K_c onto the molecule-fixed a and c axes as defined in Figure 1, respectively, and the projection quantum number M onto the space-fixed Z axis. In the molecule-fixed coordinate system exchange of the proton spins corresponds to rotation of $\pi/2$ about the b axis, which is identical to a rotation of $\pi/2$ about a followed by a rotation of $\pi/2$ about c . The corresponding symmetry of the rotational wavefunction is the product of the parities, $P = (-1)^{K_a + K_c}$. This leads to *para* water requiring $K_a + K_c$ being even with an absolute ground state of $|0_{00}0\rangle$. For *ortho* $K_a + K_c$ is odd and the ground state is denoted $|1_{01}M\rangle$. The responses of the two absolute ground states to a strong dc electric field are displayed in Figure 2 a, showing the non-degeneracy of the *ortho* water M states in the presence of an electric field. The differences in the Stark effect lead to distinct effective dipole moments μ_{eff} , i. e., space-fixed dipole moments, plotted in Figure 2 b.

The force experienced by the molecules inside the electric deflection field E is proportional to $\mu_{\text{eff}} \cdot \nabla E$ [27]. The ground states of both *para* and *ortho* water are strong-field seeking (Figure 2), preventing their separation using electric focusing techniques for weak-field-seeking states [26]. The general applicability of the electrostatic deflection technique to water samples was demonstrated. [28, 29] Our combination of the deflection by strong inhomogeneous electric fields with very cold molecular beams allows for the separation of the nuclear-spin states. The quantum-state-resolved detection method allows for their unambiguous assignment. In the current experiment (see supporting information for details) a supersonic molecular beam is used to produce a cold water sample in the gas-phase

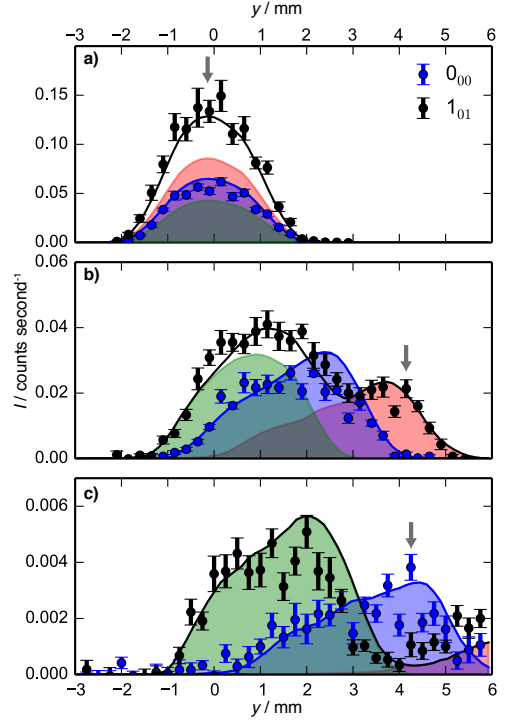


Figure 3: Measured (data markers) and simulated (solid lines) spatial profiles for water co-expanded in 40 bar of neon using deflection voltages of a) 0 kV and b) 15 kV. c) Expansion in 15 bar of argon using a deflection voltage of 15 kV. Green and red shading correspond to $M = 0$ and $M = 1$ levels of the $|1_{01}\rangle$ state, respectively and blue shading to the $|0_{00}\rangle$. Gray arrows indicate the positions at which the spectra in Fig. 4 were collected.

with a rotational temperature of 8 K, corresponding to $> 99\%$ of *para* and $> 96\%$ of *ortho* molecules in their absolute ground state, respectively. The molecular beam is then dispersed perpendicular to its flight direction according to the effective-dipole-moment-to-mass ratio (μ_{eff}/m) using strong inhomogeneous electric fields [27, 30]. Water molecules are quantum state selectively ionized via (2+1) resonance-enhanced multiphoton ionization (REMPI); a spectrum is shown in the supporting information.

Spatial profiles of the individual quantum states in the molecular beam are shown in Figure 3, with solid lines indicating corresponding trajectory simulations (see supporting information for details). In the absence of a deflection field, Figure 3 a, the *para* and *ortho* constituents of the beam are mixed and centered around the zero position.

This is confirmed by the REMPI spectrum obtained at this position, Figure 4 a, which shows the resolved resonances for both, *para* and *ortho*, ground states. Analysis of the spectrum yields a *para* : *ortho* ratio of approximately 1 : 3, consistent with a conservation of the nuclear-spin temperature through the supersonic expansion. Application of an electric field deflects the beam in the upward direction, consistent with the strong-field seeking nature of the populated states. The spatial shift depends on the effective dipole moment, and a clear separation of *para* and *ortho* water is observed. At large deflection fields the spatial profile of *ortho* water bifurcates, corresponding to the splitting of the $M = 0$ and $M = 1$ components. This is indicated by the green and red shading in Figure 3 b and c. Consistent with the calculated Stark curves and effective dipole moments, Figure 2 a and b, the $|1_{01}1\rangle$ state experiences the largest de-

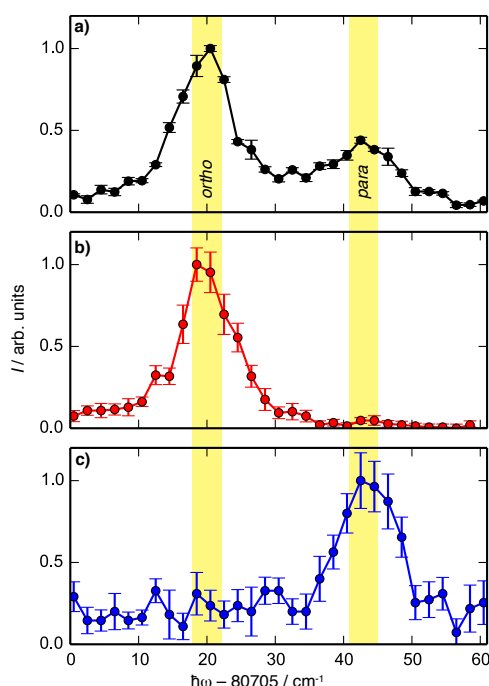


Figure 4: Rotationally resolved 2+1 REMPI spectra showing characteristic transitions for *para* and *ortho* water. a) Undeflected beam with thermal population of both spin states. b) Pure *ortho* ($|1_{01}1\rangle$) sample created in the neon expansion at 15 kV deflection voltage. c) Pure *para* ($|0_{00}0\rangle$) sample created in the argon expansion at 15 kV deflection voltage.

flection and the $|1_{01}0\rangle$ state the least deflection, with the $|0_{00}0\rangle$ *para* state in between. For water co-expanded in neon, application of 15 kV to the deflector creates a region of space, $y > 4$ mm, where only the $|1_{01}1\rangle$ state is present and a pure *ortho* sample is obtained. This is confirmed by the REMPI spectrum shown in Figure 4b. The measured purity of the *ortho* beam at this position is 97 %, primarily limited by background water in the vacuum chamber. Simulations suggest an achievable purity in excess of 99% with the present setup; see supporting information for details.

Further increasing the deflection through the use of a slower molecular beam, seeded in argon, leads to a nearly complete depletion of the $|1_{01}1\rangle$ *ortho* state and the creation of an enriched *para* $|0_{00}0\rangle$ sample, as shown in Figure 3c and confirmed by the REMPI spectrum, Figure 4c. A purity of 74 % for *para* water is measured, which simulations indicate would be increased to > 87 % if background water was more efficiently suppressed. Using a setup with two subsequent deflection stages a purity > 96 % could be obtained. The slower beam, furthermore, allows the creation of a pure *ortho* sample in the $M = 0$ angular momentum projection at a position $-1 < y < 0$ mm. This position is depleted of all other quantum states in the original beam and we obtain a > 99 % pure $|1_{01}0\rangle$ sample.

The produced pure molecular beams have densities on the order of 10^8 cm $^{-3}$ and 10^7 cm $^{-3}$ for neon and argon expansions, respectively. The latter is primarily limited by the longer gas-pulse duration and the strong deflection causing molecules to collide with the electrodes and not reaching the interaction region anymore. These densities are sufficient for precision spectroscopy or laboratory scattering experiments and should enable the study and determination of the near-degenerate “doorway states” that might be re-

sponsible for nuclear-spin interconversion according to the quantum relaxation model [6, 7].

The current experiment, at 20 Hz, allows the production of $\sim 10^{13}$ nuclear-spin-selected molecules, or 1 picoliter, per day. Significantly larger quantities could be produced using higher-repetition-rate [31] or continuous molecular beams. The current quantities are sufficient for the production of nuclear-spin-pure surface layers, for instance, highly polarizable layers of *ortho* water. The production of pure *para* water opens up possibilities for hypersensitized NMR experiments through polarization transfer *via* water addition, comparable to *para*-hydrogen induced polarization transfer (PHIP) [12, 13], but with wider chemical applicability.

The presented technique for quantum-state separation is generally applicable to polar neutral molecules and allows for the production of single-quantum-state samples, i. e., for the separation of nuclear-spin isomers.

Keywords: Isomers; Laser Spectroscopy; Quantum-State Selection; Nuclear-Spin Separation; Cold Molecules

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